

LITHOSILICATES: A NEW FAMILY OF MICROPOROUS MATERIALS

“Whenever you have a novel structure you usually get novel properties.” Edith M. Flanigen [1] (First winner of the International Zeolite Association lifetime contribution and achievement award).

Zeolites and related microporous materials contain regularly spaced molecule-sized pores and are fascinating examples of molecular engineering. More than just aesthetically inspiring, as can be seen in Fig. 1, these materials represent billions of dollars in commerce, as they have widespread industrial applications: Materials of this type are used as catalysts to produce gasoline and pharmaceuticals. For medical and industrial purposes, they are employed to separate N_2 , O_2 , and other gases. Formulated in household detergents, they remove the calcium ions that make water “hard,” replacing environmentally unfriendly phosphates. Zeolites and related microporous materials are also employed to sequester radioactive ions for bioremediation. Many new applications are being investigated in areas such as selective membranes, batteries, and fuel cells.

Properly used, the term zeolite should be restricted to naturally occurring aluminosilicates. However, related microporous materials (herein called zeolitic) have been synthesized, where elements such as B, Be, Cr, Fe, Ga, Ge, Mn, P, Ti, and Zn substitute for tetrahedrally bonded Si or Al. These atoms have roughly the same bonding configurations, so they tend to adopt the same framework connectivities as aluminosilicates and thus have the same pore structures. Further, since each tetrahedral (*T*) atom is linked by four oxygen atoms, the frame-

work must have a generalized chemical formula $[TO_2]_{1-x}^m[T'O_2]_x^n$ where the charge on each tetrahedral unit (*m* or *n*) is typically zero or -1. Additional extra-framework cations, such as H^+ , Na^+ , Li^+ , or Ca^{2+} , are then needed to balance charges. The number and nature of these cations is significant as cations are often the chemically active site for interactions with guest species, or their presence may affect the framework properties. Thus, they may dictate the catalytic or sorptive properties of the material. Empirically, the most negatively charged zeolitic frameworks that have been found, *e.g.*, those that have the largest number of extra-framework cations, are materials with formula $M^+[SiO_2][AlO_2]^{-1}$. Pauling’s rules, restated in the zeolite field as Lowenstein’s rule, dictate that the ratio of Al:Si cannot exceed unity, limiting the cation fraction to 1/7 the total number of atoms.

A new class of materials that have Li incorporated as a *tetrahedral framework species* has recently been discovered [2,3].

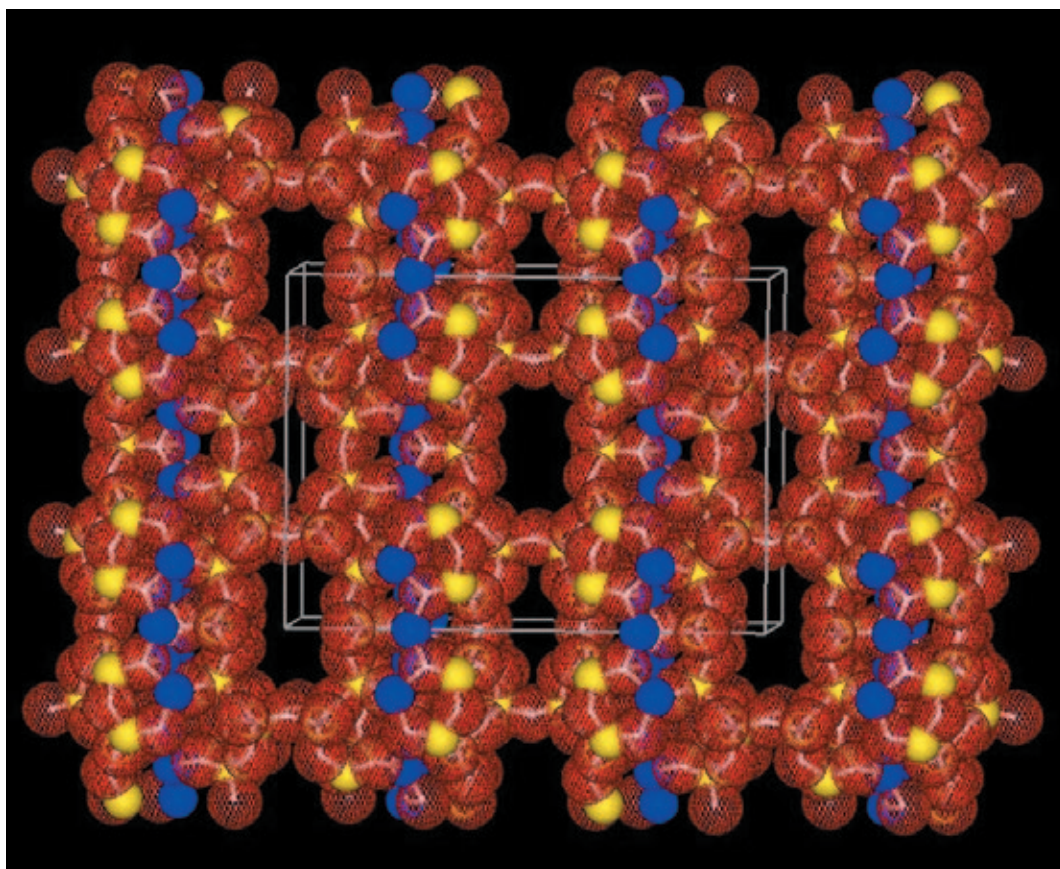


FIGURE 1. The RUB-29 framework. Tetrahedral Si and Li atoms are shown as solid yellow and blue spheres, respectively at their approximate covalent radius (1 Å). Framework O atoms are shown as transparent red spheres at their approximate Van der Waals radius (1.4 Å). Extra-framework species are omitted for clarity.

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These materials, called microporous lithosilicates, are novel for two reasons. One is that $[\text{LiO}_4]$ tetrahedra appear more flexible than other $[\text{TO}_4]$ tetrahedra. This means that lithosilicates can bond in configurations that are too strained to exist for other silicates. Thus, lithosilicates offer the promise of new families of pore structures. Second, the general formula for these materials is $M_{3x}^+[\text{SiO}_2]_{1-x}[\text{LiO}_2]_x^{3-}$, so that lithosilicates have the potential to be more negatively charged than aluminosilicates, if the Li:Si ratio exceeds 1:4.

A team of NCNR scientists and collaborators has recently completed the first complete structural characterization of a microporous lithosilicate, RUB-29. To determine the framework geometry, synchrotron diffraction measurements were performed at the NSLS using an extraordinarily small single crystal — with dimensions $10\text{ }\mu\text{m} \times 10\text{ }\mu\text{m} \times 2\text{ }\mu\text{m}$. (For comparison, human hair is typically $50\text{ }\mu\text{m}$ to $100\text{ }\mu\text{m}$ thick.) With 35 symmetry-unique atoms comprising the framework, RUB-29 is one of the most complex zeolitic structures. Powder neutron diffraction at NIST was then used to better determine the siting of the framework Li atoms, as well as four additional extra-framework Li atoms and seven other extra-framework species. The RUB-29 framework is shown in Fig. 1.

The structural studies of RUB-29 demonstrate two novel structural building blocks, a Li,Si-spiro-3,5 and a Li,Si-spiro-5 unit (see Fig. 2). It should be noted that both these building units contain

“three-rings” where three T atoms, in this case one Li and two Si atoms, are bonded in a cyclic structure. This three-ring structural entity is highly strained in silicates; only one silicate example has ever been found.

In RUB-29, only 1 in 5 T atoms are Li, so the total framework charge is comparable to 1:1 aluminosilicates. However, RUB-29 appears to be stable under conditions where these high-aluminum zeolites tend to degrade. Further, there is promise that new lithosilicate materials can be synthesized with even higher Li:Si ratios.

Another interesting property exhibited by RUB-29 is that the Li atoms, both in framework and non-framework sites, appear to move on an NMR timescale at temperatures as low as $250\text{ }^\circ\text{C}$. Much more work is needed to learn about conduction in this material, but it may hold promise for ionic conduction applications, such as in batteries.

REFERENCES

- [1] S. Borman, R. Dagani, R. L. Rawls, and P. S. Zurer, *Chemical & Engineering News*, January 12, 1998.
- [2] S.-H. Park, P. Daniels, and H. Gies, *Microporous Mater.* **37**, 129 (2000).
- [3] S.-H. Park, *et al.* *Journal of the American Chemical Society* (2000), in press.

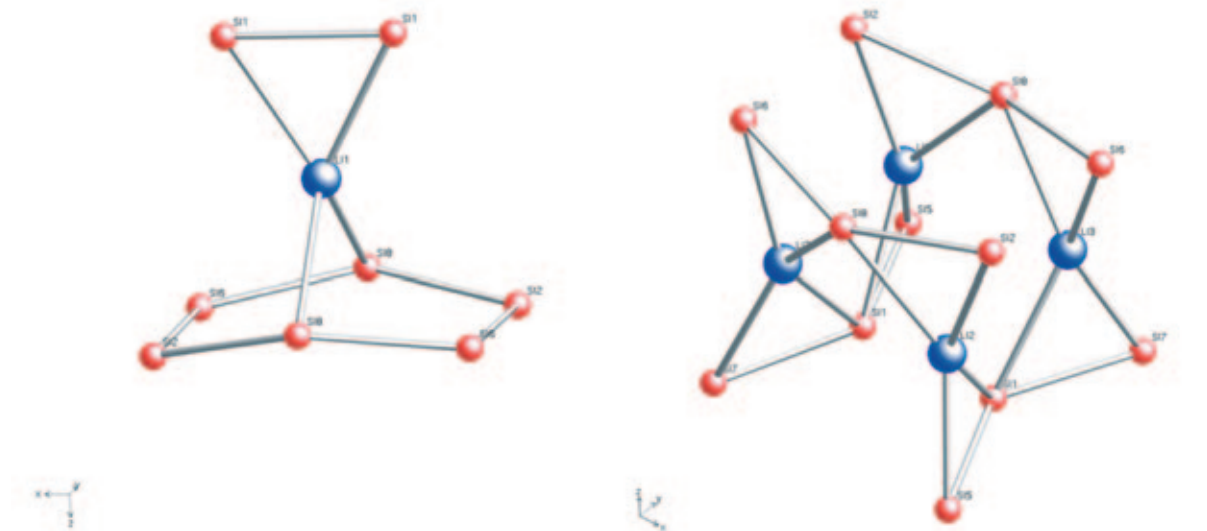


FIGURE 2. Li,Si-spiro-3,5 (left) and Li,Si-spiro-5 (right). Small red circles indicate the centers of $[\text{SiO}_4]$ -tetrahedra, and big blue circles are those of $[\text{LiO}_4]$ -tetrahedra. The O atoms that bridge each pair of Si and Li atoms have been omitted to improve clarity.